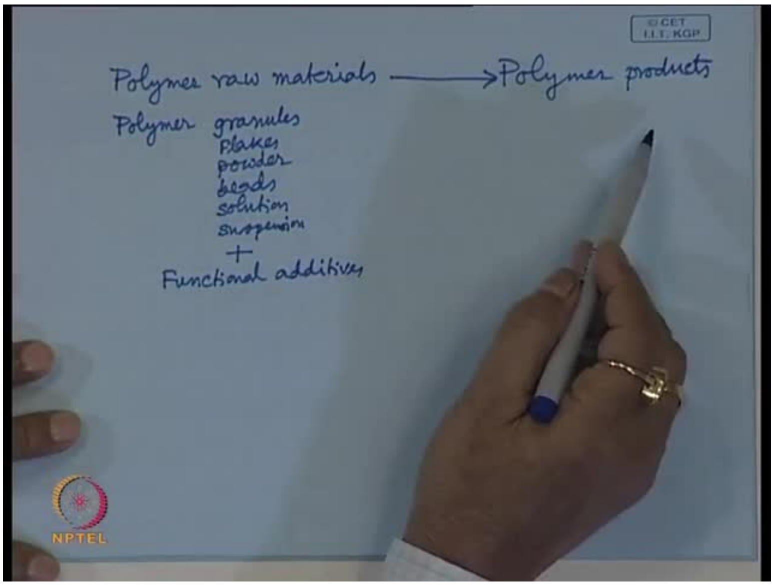
Science and Technology of Polymers
Prof. Basudam Adhikari
Material Science Centre
Indian Institute of Technology, Kharagpur

Lecture - 15
Polymerization Techniques

(Refer Slide Time: 00:38)



Polymer raw materials ⟶ Polymer products

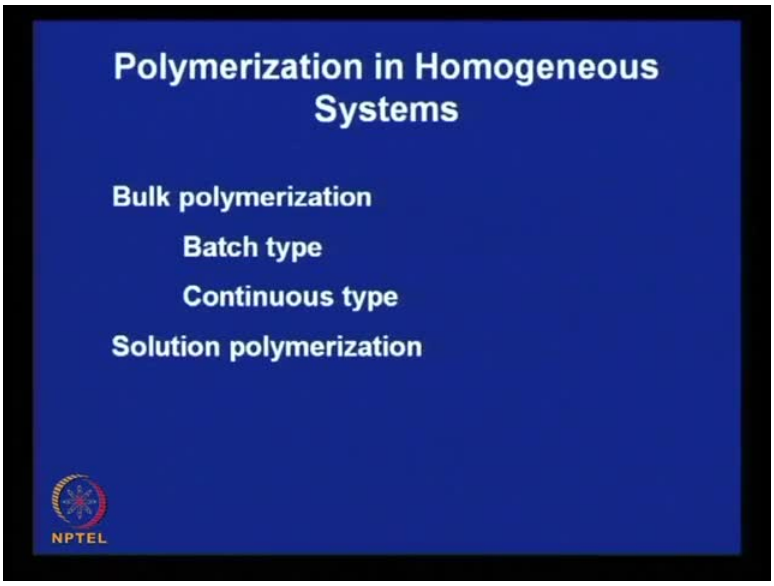
Polymer granules
flakes
powder
beads
solution
suspension
+
Functional additives

Good morning, today we are going to start these techniques of polymer manufacture. You know polymers, polymer products are made from polymer raw materials. Polymer raw materials, I mean polymer raw materials I mean polymer in the form of granules, flakes, powder, beads, solution, suspension, suspension. So, the polymers raw polymering materials are available in these forms. These are blended with functional additives to manufacture polymer products. These polymer raw materials in along with the functional additives, they are mixed together to form a polymer compound.

Then this that polymer compound subject to each other, is subjected subjected to various fabrication techniques, processing and fabrication techniques to get the polymer products. We shall discuss that part later. Today, we are going to discuss how these polymer raw materials particularly this basic polymer in the form of granules, flakes, powders, beads, solutions, suspensions. They are made in industrial or commercial scale.

Now, there are techniques of polymer manufacture.

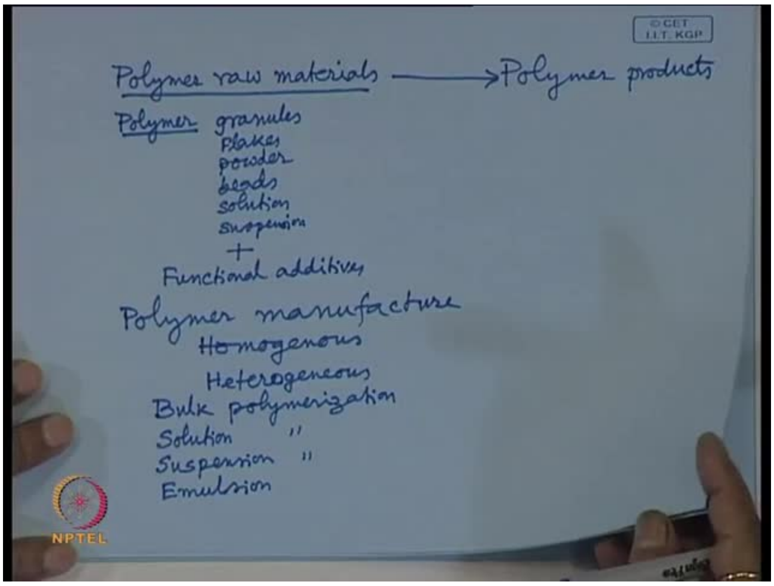
(Refer Slide Time: 03:18)



Polymerization in Homogeneous Systems

Bulk polymerization
  Batch type
  Continuous type
Solution polymerization

(Refer Slide Time: 03:24)



© CET
I.I.T. KGP

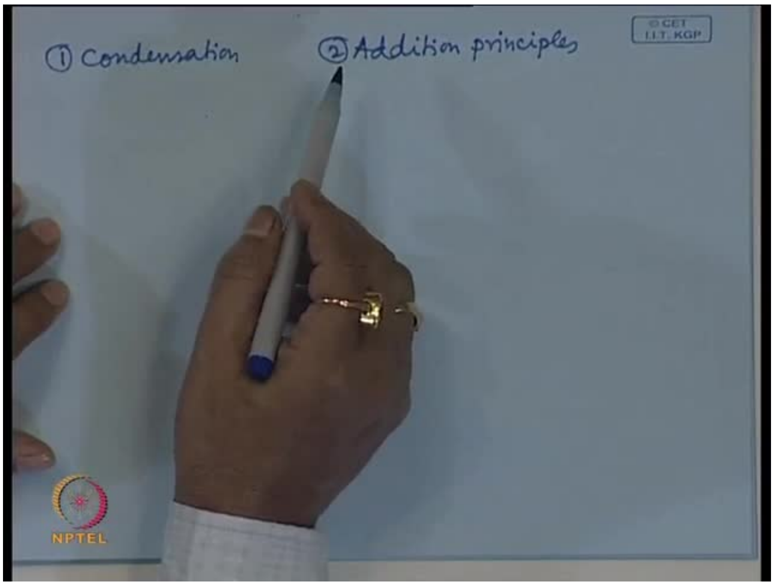
Polymer raw materials → Polymer products

Polymer granules
  flakes
  powder
  beads
  solution
  suspension
  +
Functional additives

Polymer manufacture
  Homogenous
  Heterogeneous
Bulk polymerization
Solution "
Suspension "
Emulsion

Polymer can be manufactured by homogenous system as well as heterogeneous system. Sometimes this manufacturing system maybe initial, initially homogenous, but afterwards in later stage it become heterogeneous. We shall discuss those things and out of this homogenous and heterogeneous system in general we can say, there are techniques like bulk polymerization, solution polymerization, suspension polymerization and emulsion polymerization. You know there are two major different principles of polymer synthesis condensation polymers.

(Refer Slide Time: 04:59)



Condensation principle and addition principle. Note both of these principles can be applied for making or for manufacturing polymer using this bulk technique or solution technique suspension or emulsion technique. It depends on the characteristics of the polymerization reactions. You have seen that condensation polymers are synthesized using monomers and it occurs in various intermediate steps. This polymerization is not highly exothermic, it is less exothermic polymerization system whereas, addition chain polymerization is highly exothermic polymerization.

Why I am telling this thing because in industrial manufacture huge batch is involved, that means huge quantity of monomers and other ingredients, those are charged to the reactor for manufacture of the polymer. You have seen in a simple laboratory synthesis of a chemical compound. You need a container, in that container you take the monomer or the reactants. You add the ingredients provide sufficient conditions of environment. Say either inert environment or in presence of air. Then you have to raise the temperature of the reaction vessel to the level of the activation energy.

So, that reaction starts and continues after that simultaneously. It needs stirring agitation, agitation of the mass. That is a very small quantity maybe 50 grams or 50 milliliter or 100 grams or 100 milliliter be it in liquid form or solid form, there stirring is very easy. Now, in the laboratory synthesis of polymer you can use a simple magnetic stirrer. I think you have seen, what is magnetic stirrer? It is nothing but a plate below which there is a motor which is fitted with a magnet. On the top of the plate, if you place your vessel and inside the vessel, if you keep a magnetic bar, magnetic bar means a iron bar coated with teflon or other inert polymer, then if you rotate the magnet below the plate of the magnetic stirrer.

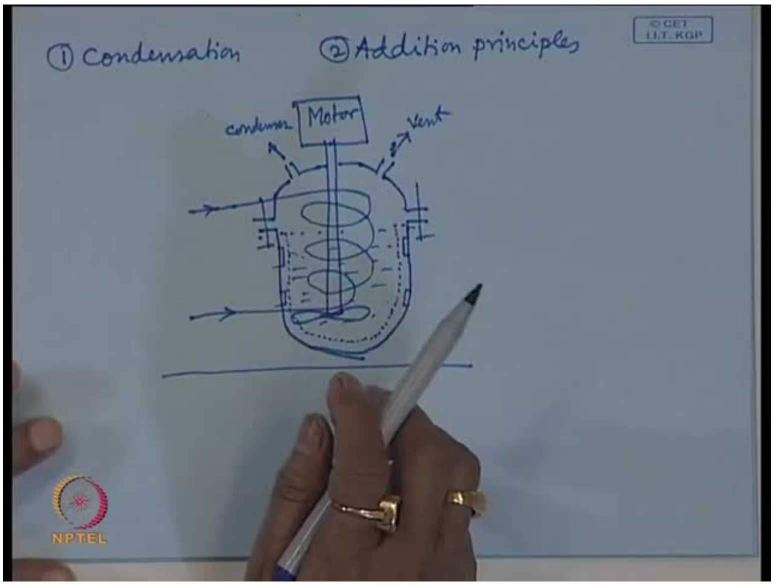
So, that we will rotate the inside magnetic bar inside the polymerization vessel or reaction vessel, so this way you can stir or there are available mechanical stirrers. Say if the batch size is bigger than that which cannot be controlled or accommodated by that magnetic stirrer, then we need a mechanical stirrer, laboratory scale mechanical stirrer. That mechanical stirrer is fitted with a motor and on one side, the strap of the stirrer is fitted with a motor and on the other end there is a blade is fitted, a blade of different design set, that is fitted there. It rotates by electrical operation and we can get the stirring.

In industrial scale that stirrer is huge stirrer. Then control of temperature in case of laboratory synthesis, what you do? You can use a heating mantle, have you seen heating mantle? It is a container it is a container of different volume, where you can place your round bottom flask of say 100 millimeter milliliter to 1 liter or more. Within that mantle that electrical heater elements are there, so you can change the temperature with the help of a temperature controller. So, this way you can supply the heat to the to the reaction vessel and carry out the polymerization or any other reaction. In case of industrial polymerization, what happens?

You have to supply the heat either by electrically or by hot gas or by hot oil and here the heat transfer surface is very much important. Heat transfer surface means you have to supply the heat to the container or the reactor, so that the entire mass is homogenous homogeneously heated, that means the temperature becomes uniform within the reactor.

So, the simple mantle type heating system is not there. So, there may be heating coil heating coil or other systems, which can supply the heat to the polymerization vessel.

(Refer Slide Time: 11:20)

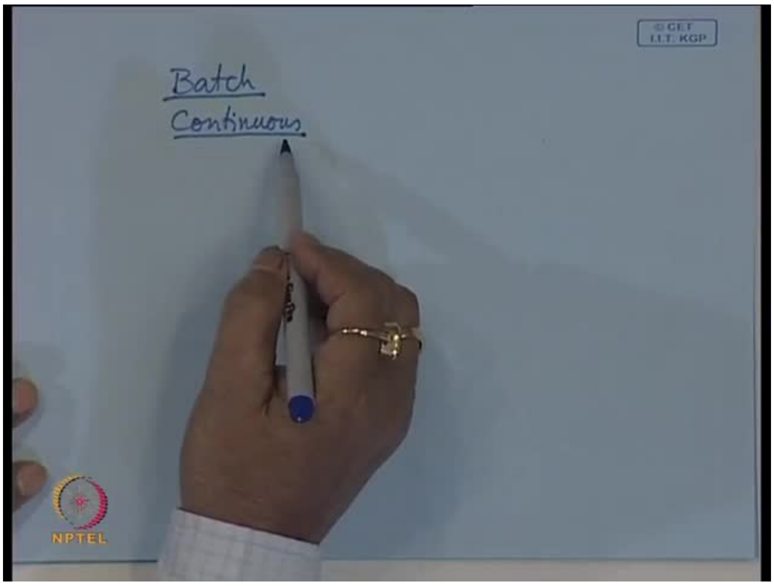


It may look like this say… Say this maybe a simple sketch of a reactor. Now, this is a huge stirrer, huge stirrer which is fitted with the motor. Then that maybe a sorry, that maybe a vent, this may be connected to a condenser, such a so and so. Inside there can be vapor, anything. See if you look at some typical reactor designs and other things you can see of these things. So, within this reactor monomer and other things they are charged, then heat is supplied either by electrical heating say you can consider this as electrical heating coil or it can be a tube, it can be tube through which hot oil or hot gas, which is passed through this coil and it heats the…

Actually I am little wrong, I should show this coil from there. So, actually it remains immersed in this liquid inside this kettle. So, heat is supplied, here is the heat supplier surface. The surface of this tube, surface of this tube and provides the heat transfer surface. Not only that there may be jacketed heating by outside jacket outside jacket. Again the thermal conductivity of the material of the reactor is plays an important role there, from outside jacket is heating. I have not shown here, so that is also used not only that the outside jacket can also be used for cooling system.

Not only that this same heating system can be used as cooling system also, if you pass some fluid through this hot fluid, so this tube sometimes you can pass also cold fluid. So, this way it can keep the temperature controlled inside the reactor. Now, we are going to discuss this bulk polymerization, say batch type bulk polymerization continuous type. Now, batch type you do not know, what is batch type?

(Refer Slide Time: 15:38)



Now, this polymerizations or chemical manufactured both these can be carried out by batch process or continuous process. There are advantages of both these techniques again with serious disadvantages too. I mean that in case of batch process, the productivity is less. Whereas, in continuous process the productivity maybe high. In order to get higher productivity higher amount of polymer manufacture in short period, one can one should go through continuous process.

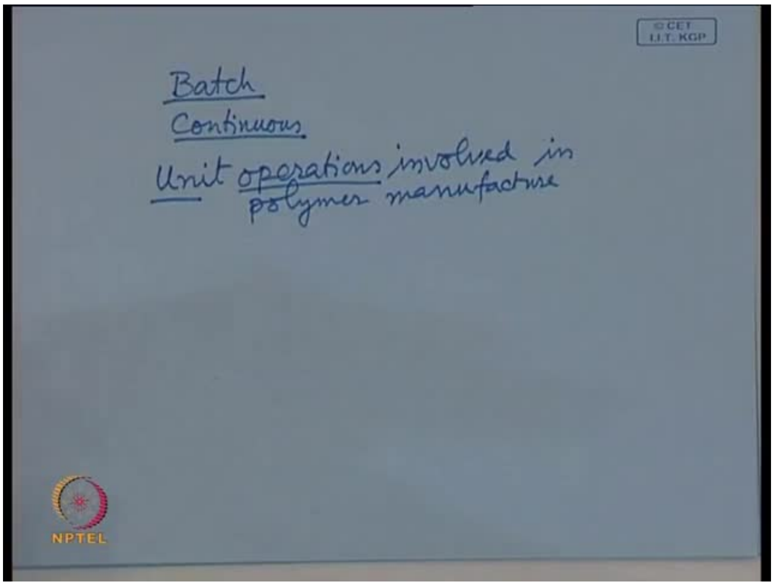
Whereas, in a batch process the reactor have shown, see that is a batch reactor, where you have to a give a charge, say one time charge of monomer and other ingredients. Then supply the sufficient conditions and polymerization starts and continues. After the polymerization is over, that means after suitable level of conversions say 60 percent or 70 percent conversion, you have to stop the polymerization, then you have to remove the mass from the reactor. After removing the mass from the reactor, you have to isolate the unreacted monomer and other ingredients present over there to get the polymer.

So, that in that actually needs more time, so the productivity this could total quantity of polymer manufactured per day will be less. Whereas, in a continuous process, if this monomers has continuously failed to the reactor in one side and from the other side, if the product is collected then there will be higher productivity. But the problem is in continuous process one cannot go to higher conversion. Higher conversion is not possible, higher conversion I mean you can get high molecular entire product.

But the conversion maybe 20 percent, 30 percent because there are problems like viscosity and other things, handling of this entire mass. So, it is carried out up to lower conversion and then they they are need say provision for recycling isolation, separation, isolation, purification of the unreacted ingredients and those isolated, separated and purified unreacted ingredients again they need to be recycled to the initial or the recycled to the reactor. Again batch, in batch reactor there may be only one vessel which is used for polymer manufacture.

In continuous reactor process, a series of reactors in a battery like say battery of 10 reactors, maybe connected in series. In each reactor, the conversion may be less, so when it comes out of the last reactor you can find a higher conversion. Then it needs some units of separation, isolation, purification etcetera. From there again we have to recycle the unreacted ingredients to the first reactor and it goes on continuously. So, from one side you are feeding the monomer and ingredients from the other side we can get the polymer.

(Refer Slide Time: 19:47)



Batch

Continuous

Unit operations involved in polymer manufacture

Here, actually on polymer manufacture there are certain unit operations. Unit operations, various unit operations are involved. Probably you have heard these two words unit operations. These unit operations are the subject matter of chemical engineering. Say unit operation maybe mass transfer, heat transfer, separation, purification, distillation, size separation, your size deduction; like casing, grinding all these things. Purification maybe distillation stripping etcetera, so those unit operations if time is available, I shall cover in one lecture later not today.

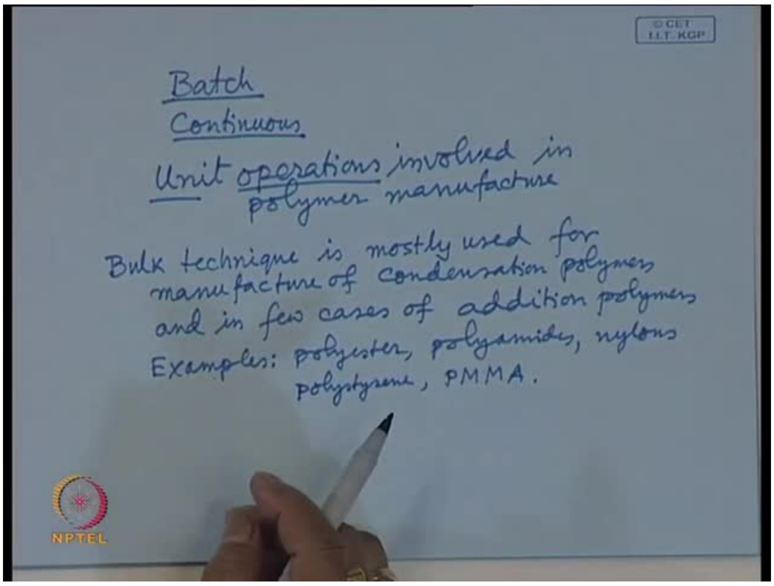
Coming, so this all these polymer manufactures, they involve unit operations for getting high productivity of this polymer, higher quantity of this polymers, desirable quantity of this polymers. Now, you have asked a question like, why a condensation polymers are less exothermic? You think of the polymer synthesis by the condensation process where it it occurs in various steps. It is a slow process, it is a slow process and very slow process and there may not be, there may not be very large number of sites where these slow steps are occurring in one time. Because you know this polymerization reactions depends on the position factor.

I told you out of 10 to the power 13 conditions, only one condition maybe reactive for carrying out this reactional polymerization. So, this condensation polymerization is less exothermic. Whereas, in case of addition chain polymerization, depending on the initiator free radicals availability, there may be large number of polymer chains can start from the beginning and at the same time, since this kinetics is very, very fast, very fast polymerization occurs. So, all of a sudden there may be huge quantity of heat generation, so that is why we say that addition chain polymerization is highly exothermic.

So, addition chain polymerization is difficult to manage in industrial polymerization, that is why people go for tubular reactor. There are various designs of reactor, various designs of reactor. Say people use tubular reactor. Tubular reactor a narrow tube is a reactor narrow tube in a form of your spiral. That is a polymerization reactor, from one end of the tube monomers are introduced and from the other end polymers are collected. So, that helps you higher heat transfer area. See in a gas phase polymerization, polythene manufacture, polypropene manufacture, in gas phase polymerization, it provides higher heat transfer area.

So, since it provides higher heat transfer area. So, if that surface is covered with coolant, then exothermic heat generated in the polymerization reactor can be easily removed. Now, let us see what is bulk polymerization? Bulk polymerization is a technique mostly used for condensation polymers.

(Refer Slide Time: 24:46)



Batch

Continuous

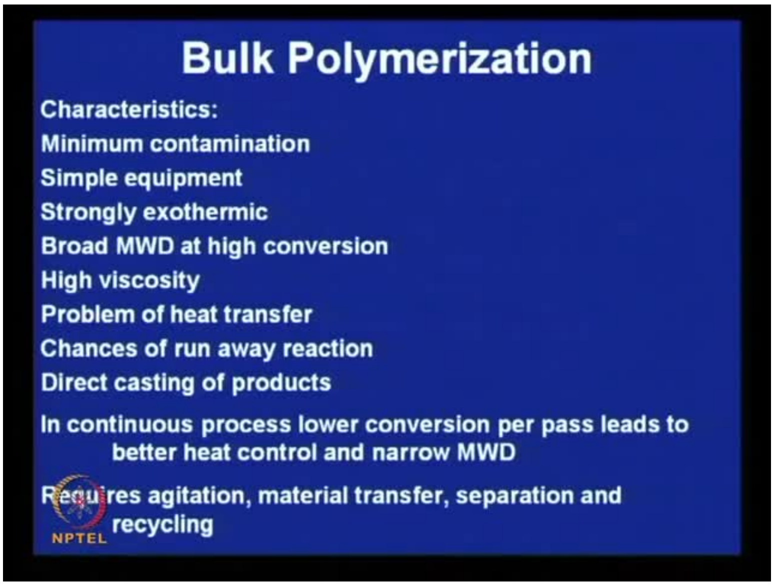
Unit operations involved in polymer manufacture

Bulk technique is mostly used for manufacture of condensation polymers and in few cases of addition polymers

Examples: polyester, polyamides, nylons polystyrene, PMMA.

Bulk polymerization is a technique mostly used for condensation polymer and in few cases of addition polymers. Examples maybe; polyester, polyamides, nylons etcetera and in case of addition chain polymers say polystyrene, PMMA. What is bulk polymerization?

(Refer Slide Time: 26:17)

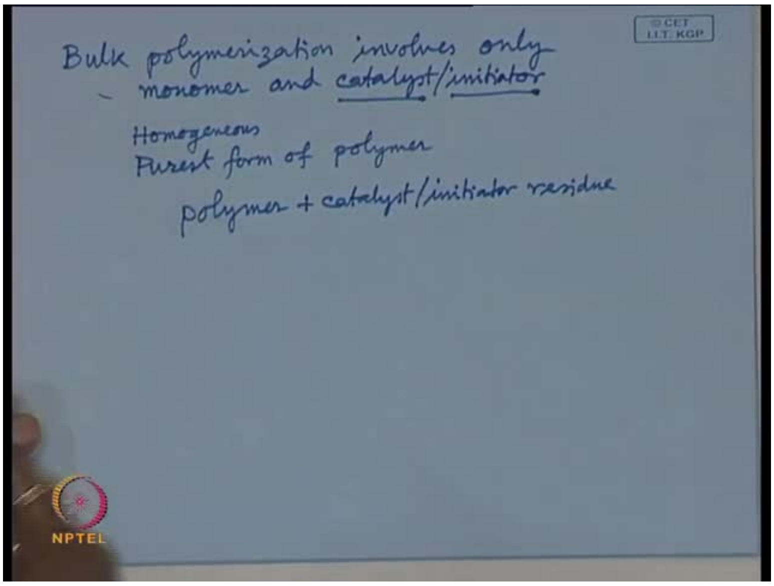


Bulk Polymerization

Characteristics:
Minimum contamination
Simple equipment
Strongly exothermic
Broad MWD at high conversion
High viscosity
Problem of heat transfer
Chances of run away reaction
Direct casting of products
In continuous process lower conversion per pass leads to better heat control and narrow MWD
Requires agitation, material transfer, separation and recycling

It is a it is a heterogeneous system. Bulk polymerization falls under the category of hetero a, sorry homogenous polymerization system homogenous polymerization system.

(Refer Slide Time: 26:35)



Bulk polymerization involves only
- monomer and catalyst/initiator

Homogeneous
Purest form of polymer
polymer + catalyst/initiator residue

Bulk polymerization involves only monomer and catalyst or initiator, depending on the nature of polymerization. In case of condensation polymerization, we use catalyst. In case of addition chain polymerization, we use initiator. This bulk polymerization is homogenous system and we get purest form of polymer very high. If we need very high quality polymer, then we should go through this bulk polymerization technique. Because after the polymerization, what will be the composition?

Polymer polymer plus catalyst or initiator residue. In case of addition chain polymer, there may not be any initiator chain residue in bulk polymerization, because of all the initiator molecules decomposed that will add to the polymer chain. If we can allow sufficient time and condition, then entire monomer can be converted to polymer. So, in the product the raw polymeric product will be obtained that is only the polymer, no initiator residue no other impurities. In case of condensation polymerization, you know there is some by product, which is eliminated and that is removed from the polymerization system.

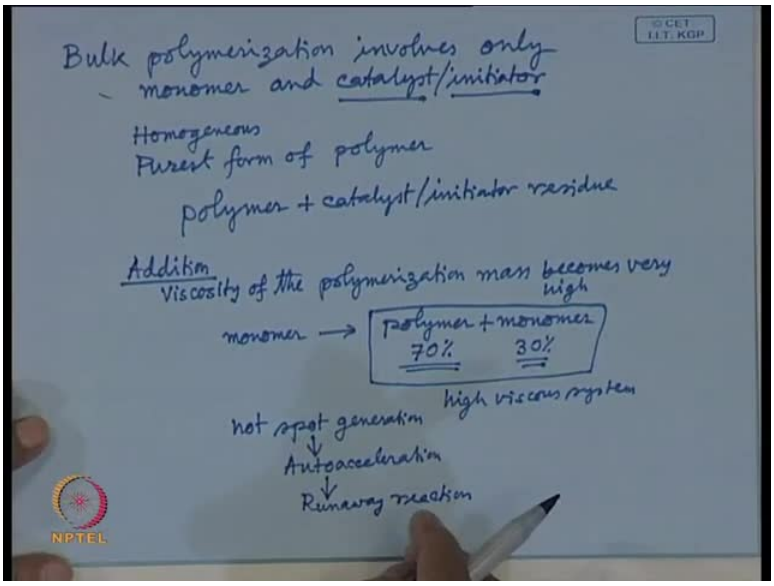
So, that is also not present as impurity not only that catalyst, which is used for this condensation polymerization. That is very small quantity, so if that is not considered as impurity in the polymer mass. So, the product obtained from bulk polymerization does not require any purification step. So, bulk polymerization technique does not require any purification step or it does not require any isolation or separation of the polymer from the monomer and other impurities etcetera, but there may be problem. In case of condensation polymerization, it involves very high temperature.

When I will show you this with the help of certain flow diagram, synthesis of polyester manufacture of polyester or nylon you will see that, it involves very high temperature. Because these intermediates, the melting points of the intermediates are very high, until and unless this is not kept in a freed stage freed phase polymerization reaction cannot continue. Then it will be heterogeneous. The polymer will will remain solid dispersed in the intermediate phase. In case of condensation polymerization, in that case one cannot achieve very high molecular rate product.

So, in order to effort that both the monomer intermediates as well as the polymer of high molecular weight or higher molecular rate or higher sized polymer molecules, all remain in molten condition. So, to keep them in the molten condition, the polymerization should be carried out at high temperature, because as the molecular size increases the melting temperature increases. You have seen, is it not? If there graph, schematic diagram I showed you in earlier class, that if the molecular size increases the melting temperature also increases.

For that reason condensation polymerization, needs very high temperature for getting higher molecular weight product. Now, in case of addition chain polymerization, there are lot of problems in a huge reactor. As it is highly exothermic, what happens this polymer during its growth, huge quantity of heat is generated. It needs efficient stirring for heat transfer to cooling surface.

(Refer Slide Time: 33:03)



© CET
I.I.T. KGP

Bulk polymerization involves only
- monomer and catalyst/initiator

Homogeneous
Purest form of polymer
polymer + catalyst/initiator residue

Addition
Viscosity of the polymerization mass becomes very high

$$\text{monomer} \longrightarrow \boxed{\begin{matrix}\text{polymer} + \text{monomer} \\ \underline{\underline{70\%}} \quad \underline{\underline{30\%}}\end{matrix}}$$

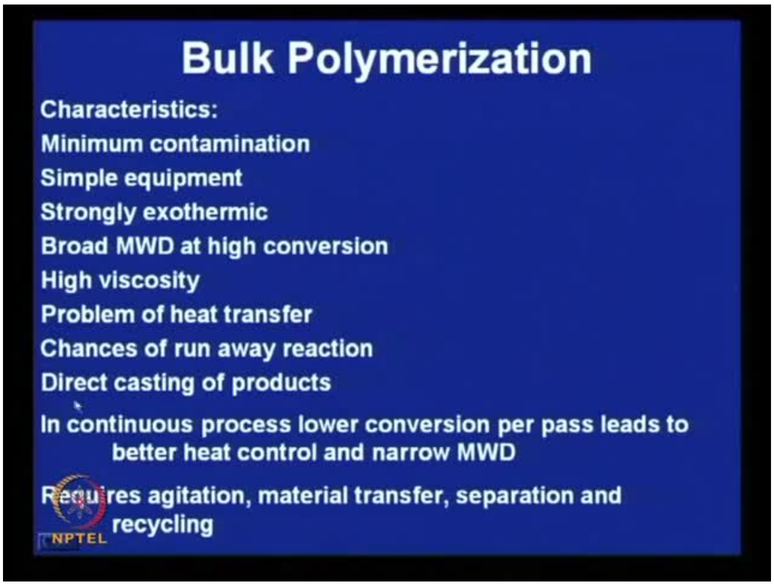
high viscous system

hot spot generation
↓
Autoacceleration
↓
Runaway reaction

Again this polymer addition chain polymer, which is formed that remains soluble in the monomer phase, because it is a homogenous system from initial starting point to the final polymerization stage. So, polymer remains dissolved in the monomer. So, in this case what happens viscosity of the it become very high because highly viscous with the with the increasing conversion. Certain percent monomer converted to polymer 90 percent remains as monomer. So, gradually if the composition changes from monomer to monomer to polymer or monomer.

Suppose, if the 70 percent conversion is there, there will be 70 percent polymer and 30 percent monomer. So, 70 percent polymer remains dissolved in 30 percent monomer. So, it gives a very high viscous, high viscous system with this. At this high viscosity, it becomes very difficult to control the temperature of polymerization, because if the heat transfers the system is not that efficient, there may be some hot spot generation. This hot spot generated, that leads to auto acceleration or gel affect. That can lead to lead to runaway reaction, means it can lead to explosion and other things. The entire batch will be destroyed, so to avoid all these things, normally in case of addition chain polymerization, if it is done in the bulk, by bulk technique it is carried out. It is actually stopped at lower conversion, say 50 percent, 60 percent like that. That means, such type of polymerization can be carried out in two steps.

(Refer Slide Time: 36:47)



Bulk Polymerization

Characteristics:

Minimum contamination

Simple equipment

Strongly exothermic

Broad MWD at high conversion

High viscosity

Problem of heat transfer

Chances of run away reaction

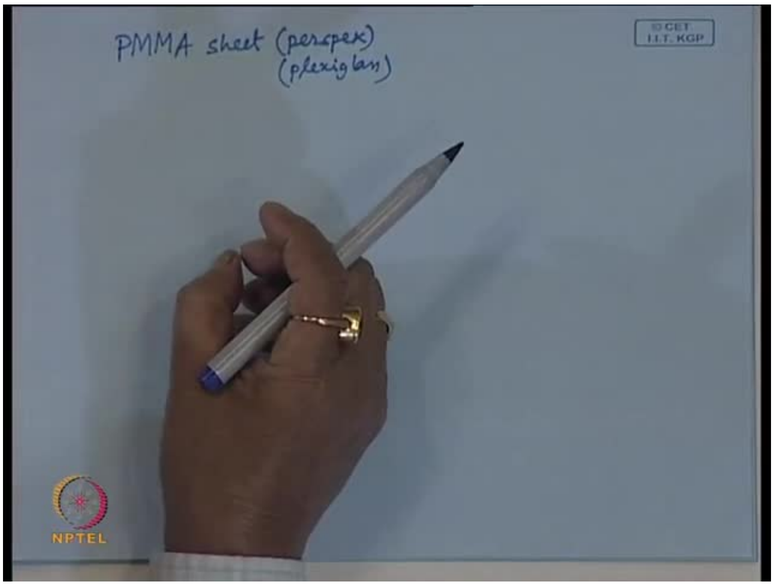
Direct casting of products

In continuous process lower conversion per pass leads to better heat control and narrow MWD

Requires agitation, material transfer, separation and recycling

You will see, where you will see that the direct casting of products, what does it mean? In order to avoid that high viscosity increase in a big reactor, so a pre polymer of lower conversion is made and that pre polymer is used for direct fabrication of product.

(Refer Slide Time: 37:30)



I think of sheet PMMA sheet or Plexiglas, these re trade names of this PMMA. How this is done? Now, first say a pre polymer up to 30 percent conversion or 40 percent conversion is made, which is a viscous solution. Then you can have a sheet mould sheet dye, it maybe 1 centimeter thick sheet, 6 millimeter thick sheet, 5 millimeters thick sheet or 20 millimeter thick sheet like that. So, that is a sheet mould that means a mould rectangular, mould having a cavity rectangular cavity in the side.

Now, this pre polymer is poured into that cavity and rest to the polymerization or conversion, say 70 percent conversion is carried out there. There you see only in that big sheet mould this one dimension is narrow, 6 millimeter, 5 millimeter, 10 millimeter or 20 millimeter, where heat transfer can be easily controlled. One can have better heat transfer, so it this pre polymer can be directly used for casting a polymer sheet. Say, you have seen these scales set square etcetera. These are directly cast product from a pre polymer of polymethyl methacrylate, where 30 percent or 40 percent conversion is carried out in the first step. In the second step that is poured into that mould and directly it is cast.

Sir, 30 percent conversion will mean that 30 percent of the individual percent is over or 30 percent of the polymer is formed?

Thirty percent monomer is converted to 30 percent polymer. Say if you take 100 gram polymer or 100 kg monomer, sorry 100 gram monomer or 100 kg monomer, if 30 kg of that entire monomer is converted to polymer, we say it is 30 percent conversion, do you understand? That means 70 percent monomer remains unreacted, in that 70 percent monomer, this 30 percent polymer remains dissolved, like a viscous solution, is it clear now? That is 30 percent conversion 30 percent conversion means, 30 gram of the initial mass, initial batch initial charge is converted to polymer.

That further leads to the further polymerization.

Yes, see in the second step within the cast mode, the residual monomer will undergo polymerization for further conversion to 40 percent, 50 percent, 60 percent to 100 percent. For example, you can taste it in your laboratory, you buy a bottle of methyl methacrylate or styrene from the market, keep on the shelf on the laboratory shelf. You do not have to do anything, allow it to pass one summer where when the temperature goes beyond 40 degree. After summer you will find the entire monomer in the bottle, as set to polymer has been converted to polymer. Then you break the bottle, you will get a PMMA or block your cylindrical block from the bottle.

If you come to my room, I will show you, I have such a block. These monomers are supplied along with some inhibitors hydroquinone. Hydroquinone is discover in the monomer, which acts as an inhibitor, which does, which prevent the polymerization during storage, handling, transportation etcetera. Still then it is so sensitive for thermal polymerization. If it is not kept in the refrigerated condition, if it is not stored in the refrigerated condition, say styrene and methacrylate, it undergoes polymerization in the bottle itself.

Even if there is any inhibitor present, but for polymer synthesis of manufacture you have to remove that hydroquinone, for getting proper polymerization kinetics, otherwise it will affect the polymerization kinetics. So, here you see in this slide, you see there are various characteristics of this is bulk polymerization. It provides minimum contamination of the polymer. As I said it contains only polymer and residual catalyst initiator. So, we can say, you can get minimum contamination in the product.

So, purest form of the polymer can be used for can be available for medical purpose by medical engineering, where purity is a criteria. There you can use this bulk polymerized polymer. Simple equivalent can provide, this bulk polymer manufacture polymer manufacture by bulk technique. Now, sometimes it is strongly exothermic for addition chain polymerization, whereas it is less exothermic for condensation chain polymerization. Now, if one goes for goes to higher conversion, then it may give broad molecular weight distribution.

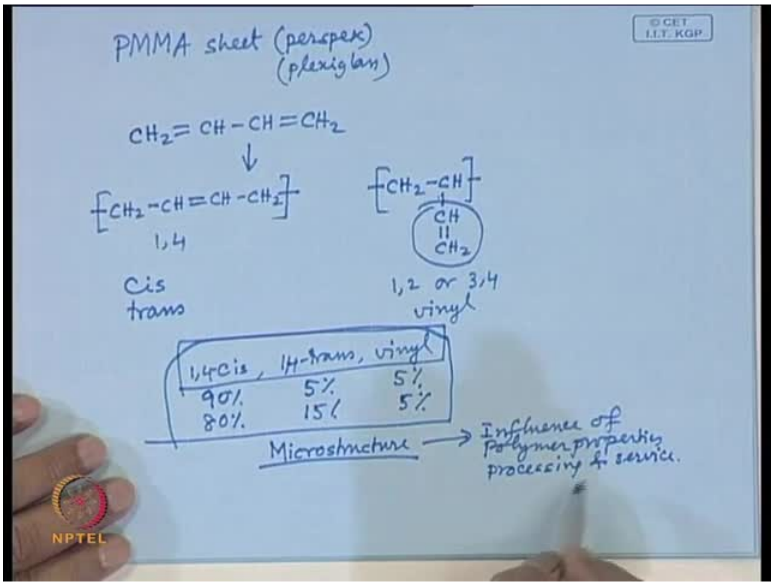
Again here is a science, underlying science in telling broad molecular distribution at a higher conversion, what is that science? As the growth occurs the mass become more and more and more viscous. If it is addition chain polymerization, even if it is condensation, chain polymerization you can say that that is a diffusion controlled polymerization diffusion control. I mean due to the polymer growth, either by condensation polymerization or by addition chain polymerization. In both the cases the reactive reacting spaces should come closer think of addition chain polymerization, a growing polymer chain for its growth.

It needs monomer at its vicinity and at the point of termination, either two such radicals come closer or one growing chain should come closer to or one any other free radical. Say maybe from your initiator etc should be should come closer to the growing chain site for termination. So, that need that is possible only if these growing chain spaces can diffuse within the mass. Now, that diffusion is restricted, get restricted by increase in viscosity isn’t it? Diffusion is restricted by increase in viscosity at higher conversions.

So, the other events of chain initiation and growth those may not get proper access to growing to higher sizes. So, that gives a broad distribution of molecular sizes. So, actually the final polymer mass, in the final polymer mass the low molecular weight fractions might be formed at the later stages. Because those low molecular weight chains, may not be able to diffuse enough through the viscous mass. That may get terminated. So, this actually this science should be understood. How that means? The reason behind this broad molecular, weight distribution at high conversion in a bulk technique to understand, that you have to look at that picture of viscosity and diffusion of the free radicals.

I said this problem of heat transfer, so I showed this schematic of that polymerization reactor where huge stirrer is used. So, with the progress of growth viscosity becomes high and heat transfer becomes a problem. That lead, that may lead to local hot spot generation and there unwanted side reaction may occur leading to polymer branch formation branching of polymer or unsaturation in the polymer etcetera. Those are possible, not only that there may be possibility of various other isomeric structures formation within the polymer mass.

(Refer Slide Time: 49:24)



PMMA sheet (perspex)
(plexiglass)

$CH_2=CH-CH=CH_2$

$\downarrow$

$-[CH_2-CH=CH-CH_2]-$ 1,4 cis trans

$-[CH_2-CH(CH=CH_2)]-$ 1,2 or 3,4 vinyl

1,4 cis	1,4-trans	vinyl
90%	5%	5%
80%	15%	5%

Microstructure → Influence of Polymer properties processing & service.

Say, think of I am telling you one example. Say butanyl butanyl, it can show various possibilities. You can get 14 linkage, you can get cis structure, cis 14, you can get trans 14, you can get 1, 2, 3, 4 linkage or (( )) vinyl. Vinyl substitute from the same monomer, so in one batch of polymerization, in one event of polymerization you can have a polymer product, which can be a mixture of 1 4 cis, 1 4 trans as well as vinyl.

Now, this composition this composition you may say, this maybe maximum. So, suppose 90 percent, it maybe 5 percent, it maybe 5 percent, it maybe 80 percent and say 15 percen, say it maybe 5 percent like this. So, overall you can say looking at this composition, we should control the microstructure polymer microstructure, that means it can vary the polymer microstructure and this polymer microstructure having influence on polymer properties during processing and service, service properties and processing properties.

Their biological characteristics will change, their mechanical properties will change, their thermal properties will change, their processing characteristics properties will change, you understand? So, as the viscosity increases, it causes problem of heat transfer causes chance, chances of runaway reaction. In order to avoid these things direct direct cast polymerization, cast fabrication of polymer product is done. It requires agitation material transfer separation and recycle in case of continuous phase polymerization.

In case of continuous phase polymerization better heat control maybe available. Sometimes narrow molecular distribution can be possible as you have seen. As in this case for high conversion broad molecular distribution in order to avoid such broad molecular distribution, one can carry out continuous polymerization. Continuous batch process where since the conversion is low in this case, low conversion per pass where molecular distribution will be narrower instead of broad. In order to get such good narrow molecular distribution and good spectrum of properties, it needs agitation and it it needs material transfer.

I mean that there may be 70 percent unreacted monomer, that 70 percent unreacted monomer should be transferred. Before that it should be separated purified and then transferred recycled to the first reactor. So, that there is no loss of monomer raw material. So, this is bulk polymerization I have covered this problems and prospects of this bulk polymerization. Once again I repeat, it gives purest form of polymer, although control over the polymerization is less. So, in this case if somebody goes by batch polymerization, batch bulk technique or bulk polymerization by batch operation, if this batch size is small there is a better control. So, here bigger batch size is not recommended and we can get a very good quality polymer.

Thank you.